A BRIEF THERMODYNAMIC EVALUATION OF PRECIPITATION MODELS IN MICROALLOYED STEELS*

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Resumo

The knowledge of the amount of microalloying elements in solution and precipitated during processing of steels is very important to properly design steel and thermomechanical processing (TMP). Models have been formulated to describe the precipitation phenomena during TMP in detail. Some of these models use simple solubility products, however, together with complex phenomenological equations to describe the changes in the steel during TMP. In this work two of these simple solubility products frequently used are compared with results calculated with computational thermodynamics. The results suggest that they are not able to predict the same values as those calculated by computational thermodynamics. If the later are correct, the simple solubility products are probably introducing excessive “correcting” factors in the phenomenological equations in order to reproduce experimental results. Furthermore, if this is the case, the ability of the models to extrapolate, a basic condition in alloy design, can be questioned..

Palavras-chave:computationalthermodynamics, microalloying, steel, precipitation, Nb.

UMA BREVE AVALIAÇÃO TERMODINAMICA DE MODELOS DE PRECIPITACAO EM AÇOS MICROLIGADOS

Abstract

O conhecimento da quantidade de elementos microligantes em solução e precipitados durante o processamento dos aços é muito importante para o projeto de liga e do tratamento termomecânico (TMP) dos aços. Existem modelos que descrevem os fenômenos de precipitação que ocorrem durante TMP e detalhes. Alguns destes modelos usam produtos de solubilidade simples, acoplados a complexas equações fenomenológicas para descrever as transformações do aço durante o TMP. Neste trabalho, dois destes produtos de solubilidade frequentemente empregados são comparados com resultados calculados por termodinâmica computacional. Os resultados sugerem que eles não são capazes de prever os mesmos valores calculados por termodinâmica computacional. Se estes últimos estão corretos, os produtos de solubilidade simples devem causar o aparecimento de “fatores de correção” nas equações fenomenológicas para reproduzir os resultados experimentais. Além disto, se isto é fato, a capacidade destes modelos de produzirem extrapolações confiáveis, uma condição importante no projeto de ligas, pode ser questionada..

Keywords: termodinâmica computacional, microligado, aço, precipitação, Nb.

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1INTRODUCTION

Microalloying steel has dramatically developed in the last decades of the XX century. This was largely due to the proper understanding of the complex effects that Nb, Tian V can have in steel, even in small quantities. One of the important feature these elements present is their good solubility in iron and the relatively high stability of their carbides and nitrides. The interplay between their effects when present in solution or when precipitated is of paramount important in understanding their effects in steel structure. For this reason, from the first relevant works in microalloying of steel, thermodynamics has played an important role in understanding the phenomena occurring and later in alloy design. However, not only the cubic nitrides and carbides of each of these elements exhibit miscibility but there is also significant miscibility of Nb, V and Ti carbides and nitrides. This has posed significant difficulties to the proper understanding and modeling of the behavior of these mixtures, presently called carbonitrides, in steels. In this work, approaches to describe the solubility of carbonitrides in steels are reviewed and compared with empirical results and results obtained by computational thermodynamics. Special emphasis is placed on the approaches that are presently integrated in process-properties modeling, since the correct prediction of dissolution and precipitation play a central role in these models. Incorrect thermodynamic models will either lead to incorrect process-property models or to improper corrections in other aspects of the model to mitigate these deviations. While some empirical approaches are reasonable to describe thermodynamics- in special when interpolating results- it is proposed that computational thermodynamics methods and models should be incorporated in process-properties modeling if these are to be used for forecasting and effective alloy design.

2 THERMODYNAMICS OF CARBONITRIDES OF MICROALLOYING ELEMENTS

Nowotny in 1963 [1] summarized important information about that transition metal carbides and nitrides. He observed that many metals, including V, Ti, and Nb form carbides and nitrides with the “NaCl” crystal structure; that some of these compounds frequently deviate from stoichiometry, being interstitial (C,N) poor; and that these carbides and nitrides frequently exhibit miscibility, not only between carbides and nitrides of the same metal (Figure 1).

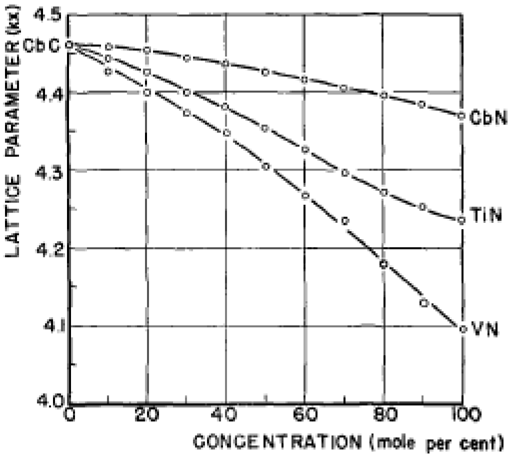

Figure 1. Lattice parameters versus composition curves for niobium (Cb) carbide-nitride systems.

Keiffer and co-workers also in the 1960´s observed that “NaCl” mixed carbides presented miscibility gaps, and reported their observations on the systems TiC-{ZrC, HfC} and VC-{NbC, TaC } [2] as exemplified in Figure 2.

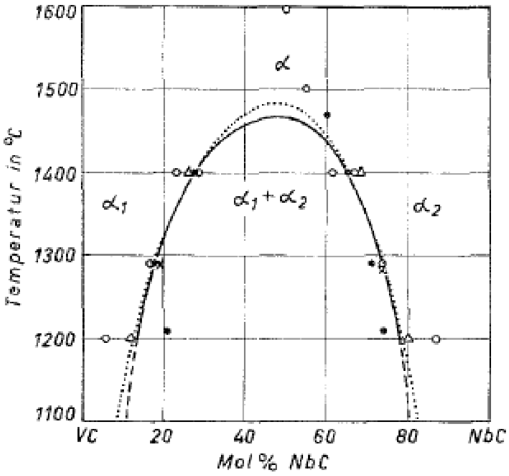

Figure 2. Miscibility gap in the VC-NbC system. Dashed line: calculated. Solid line: experimental (2).

The same group explored the miscibility of carbides and nitrides of transition metals [3]. A little after Hillert and Staffansson´s seminal paper [4] applying the sub-lattice concept to calculate the thermodynamic properties in a reciprocal system, Rudy [5] discussed the problem using carbonitrides as examples, showing the conditions for the appearance of miscibility gaps. According to Rudy [5] and Hillert and Staffansson [4] these gaps appear depending on the differences in formation energy of the end-compounds (or end-members) in the mixtures. Rudy used as an example the (Ti,Mo)(C,N) “NaCl” compounds [5]. It must be noted that in the case of microalloyed steels the thermodynamic problem is more complex as the second sublattice will also contain vacancies [1,5], thus, in general (Ti,Nb,V)(C,N,Va) would be the simplest description.

3.EQUILIBRIUM OF CARBONITRIDES WITH AUSTENITE

The relative uncertainty on the free energies of formation and mixing of these compounds and the lack of accurate information on dilute solutions of iron and Ti, V and Nb probably led to the attempts at determining the overall solubility of the carbides or nitrides in steel. Mori [6] and Smith [7,8]were pioneers in determining the solubility of Nb carbides, carbonitrides and nitrides in steels. Mori recognized the existence of carbonitrides and tried to extract the solubility product of the carbide using Smith´s solubility product for NbN. His method was one of the most adopted in the subsequent years: equilibration followed by matrix dissolution and characterization of precipitates and matrix composition. Nordberg and Aronson [9] reviewed the data on the precipitation of niobium carbide in 1968 and proposed the stoichiometry $NbC_{0.87}$ for the carbides precipitating in austenite. The following decades have seen various approaches to determine the solubility: thermodynamic calculations; chemical dissolution and separation and equilibration of steel with different atmospheres. Sharma and co-workers [10] combined their experimental measurements with an approach similar to that of [4] assuming an ideal solution of $NbC_{0.87}$ and $NbN_{0.87}$to determine the solubility of the carbonitride. Rios [11] proposed an efficient simplification to this type of model that agreed well with the data of

Mori[6] and was amenable to simpler solution methods. When discussing hot-cracking in continuous casting, Turkdogan [12] proposed an equation for the solubility product of $NbC_{0.7}N_{0.2}$ given in Equation 1.

$$\log\left(\%\underline{Nb}\%\underline{C}^{0.7}\%\underline{N}^{0.2}\right) = -\frac{9450}{T} + 4{,}12 \qquad (1)$$

This equation is currently used by Medina and co-workers in their precipitation modeling [13]. By 1994, Palmiere and co-workers[14] reviewed more than 20 attempts at the determination of the solubility product of NbC, NbN and Nb(C,N) with various fixed stoichiometries. They reviewed the limitations of the experimental methods, compared the various solubility products in the literature and presented new measurements, using atom probe to measure the precipitates and the matrix. They proposed a new formula for the solubility product, based on their atom probe measurements (Equation 2). Interestingly, they adhered to a “practical” formula of the NbC solubility product to describe the carbides in their steel. This formula has been used by these authors in recent precipitation and property evolution models [15,16].

$$log\%\underline{Nb}\%\underline{C} = 2.06 - \frac{6700}{T} \qquad (2)$$

Meanwhile, the complexity of solution mentioned by Rios [11] and other workers has been tackled by computational thermodynamics, which started developing in the early 1970´s [17]. By the late 1980´s Ohtani´s [18] assessment of the Fe-Nb-C had indicated that the stoichiometry of NbC in equilibrium with austenite depended on composition and temperature since the carbon chemical potential in the two phases must be equal in equilibrium and it is well know that small deviations in stoichiometry of compounds can have significant effects on the chemical potentials [19]. The fixed value of 0.87 [10] can be seen to be a somewhat intermediate value for low carbon steels.

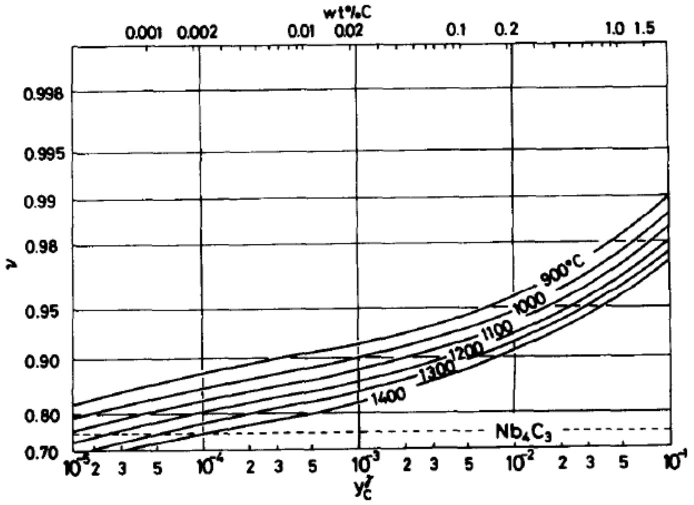

Figure 3. Stoichiometric coefficient ν (in NbC_ν) in equilibrium with austenite in the Fe-Nb-C system as a function of austenite carbon content and austenite carbon site fraction, from Ohtani and co-workers [18] assessment.

Ohtani has also assessed the Fe-C-Ti system [20] and observed similar behavior. Due the lack of data and the complexity of the systems involved, the Fe-C-N-Ti-Ni system has been assessed many times, as remarked by Lee [21]. The work of

Ohtani, Ishida and Nishizawa continued leading to the experimental work and assessment of the equilibrium austenite-(Nb, Ti, V)(C, N) by Inoue and co-workers [22]. They prepared 15 model steels and after equilibrating experiments analyzed in STEM-EDX the metals in the carbonitrides extracted by replica and determined C and N content using Vegard´s law and the measured lattice parameters in back-reflection X-Ray photographs. Figure 4 presents some of their calculated values of carbonitride compositions compared to experimental values.

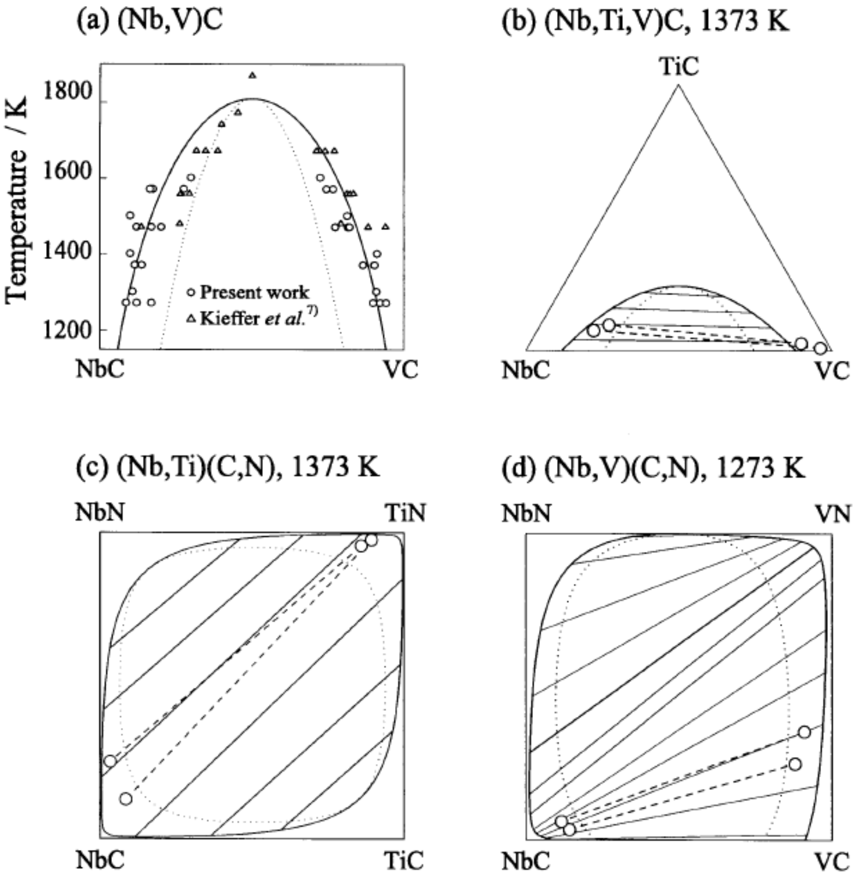

Figure 4. Experimental results of phase equilibria in complex carbonitride systems: (a) (Nb, V)C, (b) (Nb, Ti, V)C, (c) (Nb, Ti)(C, N) and (d) (Nb, V)(C, N), compared with Inoue and co-workers calculations [22].

These results have afterwards been used in other assessments such as Frisk´s [23,24]. In the work with Borggren [24] Frisk compared model results with calculations with other databases and with previous experimental results, indicating good agreement and some limitations.

4. EXAMPLES OF COMPARISON OF CALCULATIONS

As computational thermodynamics has significantly evolved in the last decades and easy to use interfaces are available for commercial software that allows them to pass results to programs in other languages (e.g [25,26]) the most relevant barrier to the use of more complex models– calculation complexity– raised by previous authors is close to being eliminated. As several models developed to predict the effects of microalloying elements in steels involve many equations, some of which involve adjustable coefficients, it is not simple to evaluate the effect of the thermodynamic information on the accuracy of the model. In this work, we present two examples comparing calculations performed with Equations (1) and (2) with those performed using computational thermodynamics. Calculations were performed with Thermo-calc[27] and TCFE9 database [28]. These calculations should provide researchers with an estimate of the deviations that can be introduced in their models by the simplified solubility product formulas and may give insight on the effect on the adjustable coefficients in other equations. Other comparisons, involving also kinetics however, can be found in [29,30], for instance.

Table 1 presents the composition of steel used in the examples of calculationscomparison to Equation 2.

Table 1. Composition (mass%) of steel used in this study

Steel	%C	%Mn	%Si	%Nb	%N
E3 [14]	0.08	1.44	0.4	0.02	0.008

In order to compare the behavior of Equation (2) and the results of computational thermodynamics, two parameters were compared. The complete dissolution temperature and the calculated %Nb%C product as a function of temperature. In the case of Equation 2 this is the solubility product of "NbC". As the results of computational thermodynamics indicate that a carbonitride with variable stoichiometry is precipitated in equilibrium in this steel, the product has no special meaning in these calculations. Computational thermodynamics indicated that the carbonitride dissolves completely at 1129°C while Equation (2) indicates complete dissolution at 1106°C. Figure 4 compares the product of the carbon and niobium content in austenite determined with the two methods.

To further clarify the reason for these differences the equilibrium carbonitride composition and its volume fraction were calculated and are presented in Figure 5, together with the values of %Nb, %C and %N in solution in austenite.

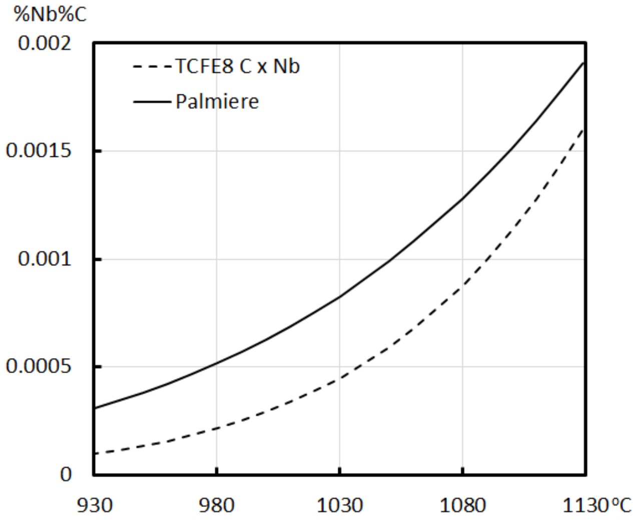

Figure 4. Comparison of the product of %Nb and %C contained in austenite as a function of temperature calculated according to Equation 2 and using Thermo-calc and TCFE9 database for steel E3 in Table 1. (Values calculated slightly beyond solubility limit)

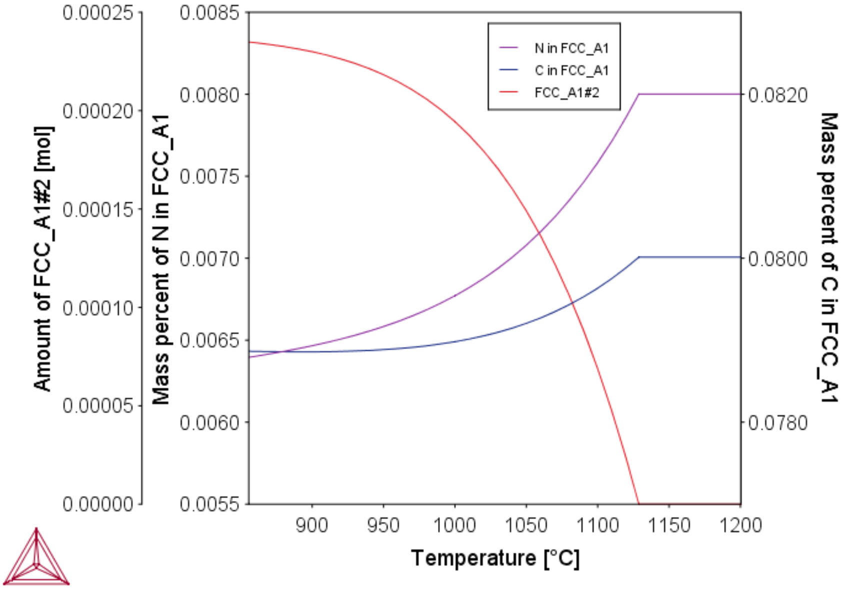

Figure 5(a). %C and %N in austenite and amount of Nb(C,N) formed in equilibrium in steel E3 as a function of temperature, calculated with Thermo-calc and TCFE9.

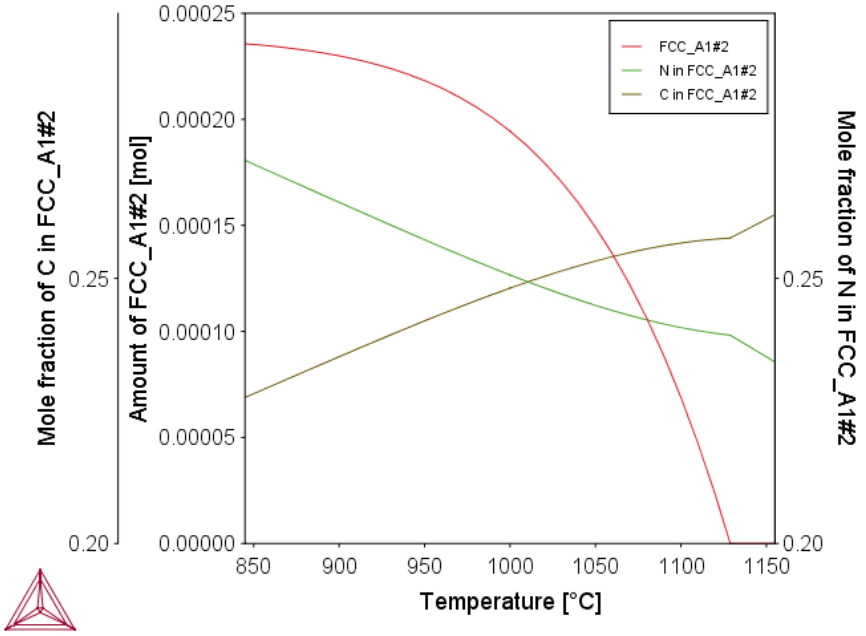

Figure 5(b) Calculated amount of Nb(C,N) and C and N contents in the carbonitride in equilibrium in steel E3 as a function of temperature, calculated with Thermo-calc and TCFE9.

The results in Figure 5 clearly indicate that, according to the computational thermodynamics calculations, the precipitate has a significant amount of N. This can be seen not only in Figure 5(b) but also in Figure 5(a), observing the composition of austenite as the precipitate is formed. It would appear that approximating the carbonitride stoichiometry as "NbC" is not a good option in this case.

As the solubility product equation proposed by Turkdogan (Equation 1) includes carbon and nitrogen, the comparison is a little more complex. Figure 6 shows a schematic plot of Equation 1 at 1000°C.

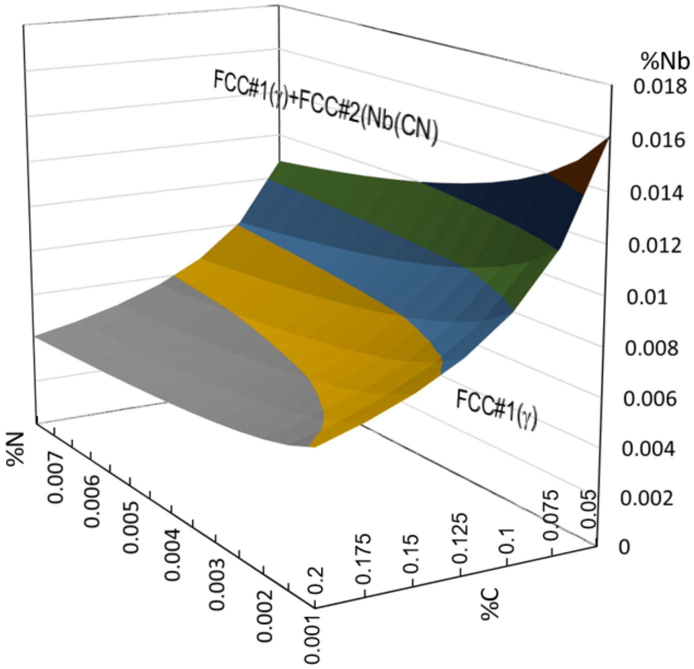

Figure 6. Calculate solvus surface for Nb(C,N) (FCC#2) in austenite (FCC#1) at 1000°C according to Equation 1.

To compare Equation 1 with the results of computational thermodynamic calculations iso-%Nb lines from the diagram of Figure 6, projected on the %N%C (base) plane, were plotted.

Figure 7 presents the comparison for a steel containing 0.5%Mn.

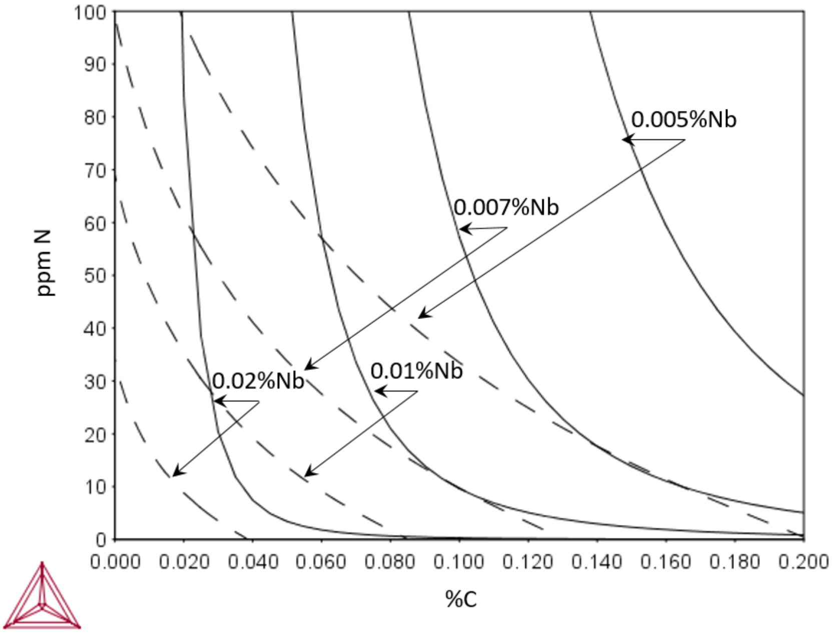

Figure 7. Comparison of austenitecontent of N, C and Nb in equilibrium with niobium carbonitrideat 1000°C. Solid lines calculated according to Equation 1 and dashed lines using Thermo-calcandTCFE9.

One of the main reasons for the evident discrepancy of the curves in Figure 7 is the fact that Equation 1 uses a fixed C/N ratio, while computational thermodynamics determines the equilibrium C/N ratio for each condition, as shown in Figure 8.

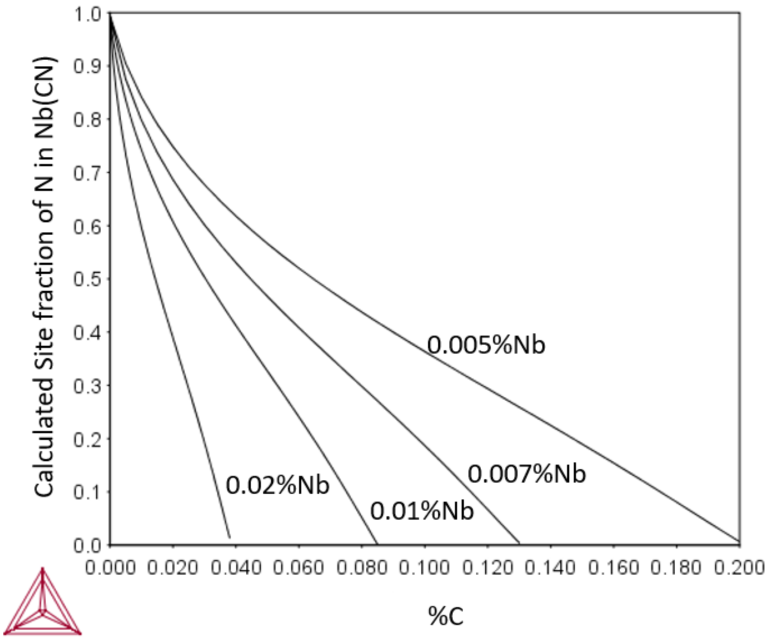

Figure 8. Calculated site fraction occupied by N in Nb(C,N) for different Nb and C content in austenite. As the sum of site fractions of C and N is approximately one (low vacancy content) the C/N ratio varies significantly for different steel compositions.

The results in Figure 7 indicate that the solubility products calculated according to the computational thermodynamics differ significantly from those calculated by Equation 1. One of the reasons is the fact that Equation 1 assumes a constant C/N ratio of 0.7/0.2, while the computational thermodynamic model takes in account the variation of this ratio.

While the use of simple solubility products (Equations 1 and 2) have clear limitations, the direct use of computational thermodynamic calculations is not without its problems, either. If the precipitates are in equilibrium with the matrix at the calculation temperature (i.e., if the composition is the equilibrium one) the predictions of computational thermodynamics should be very close to reality, in view of the large body of data supporting the assessments used in the database. If, however, the precipitation occurs during cooling or at another temperature, one can expect that either the carbonitrides will not be homogeneous in composition [30] or will have a composition that is close to equilibrium at the precipitation temperature. So, the direct application of this method also has limitations.

However, one should question, at this point, if models for prediction of microalloyed steels structure evolution should rely more on computational thermodynamics and related techniques (such as diffusion simulation e.g. DICTRA [27]or precipitation simulation e.g. PRISMA[31]or similar [32]) than on further empirical development of classical models. One interesting example is the modification proposed by Medina and co-workers [13] to the classical Dutta and Sellars [33]precipitation equation for carbonitrides in microalloyed steel. (Equation 3).

$$t_{0.05} = A\varepsilon^{-\beta} D^{s} Z^{r} exp\left(\frac{Q_{diff}}{RT}\right) exp\left(\frac{B}{T^{3}(log\, k_{s})^{2}}\right) \qquad \text{Equation 3}$$

The equation proposed by Dutta and Sellarsis based on classical nucleation theory [34], with some small modifications. Medina and co-workers, however, made the coefficients A and B in Equation 3 also dependent on the solubility product (or on the supersaturation), deviating significantly from classical nucleation theory. It is known that present precipitation simulation modeling software still rely on the adjustment of some hard to measure properties, such as surface energy [35]. However,one could argue that, by following as close as possible theoretical models, the chances of having models that will properly extrapolate and offer good development perspective in the future might be better than e introducing additional empirical factors in fundamentally sound formulas. Evidently, these models are not without merit, as they are very important for the control and improvement of process and alloys within the scope they are developed.

6. CONCLUSIONS

The knowledge of the amount of microalloying elements in solution and precipitated during processing of steels is very important to properly design the steel and the thermomechanical processing (TMP). Models have been formulated to describe the precipitation phenomena during TMP in great detail. These models use simple solubility products, however, together with complex phenomenological equations to describe the changes in the steel during TMP. The comparison of two of these simple solubility products with results calculated with computational thermodynamics suggest that they are not able to predict the same values as those calculated by computational thermodynamics. If the later are correct, the simple solubility products are probably introducing “correcting” factors in the phenomenological equations in order to reproduce experimental results. Furthermore, if this is the case, the ability of the models to extrapolate, a basic condition in alloy design, can be questioned.

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